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Semiclassical calculation of cumulative reaction probabilities

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Calculation of chemical reaction rates lies at the very core of theoretical chemistry. The essential dynamical quantity which determines the reaction rate is the energy-dependent cumulative reaction probability, $N(E)$, whose Boltzmann average gives the thermal rate constant, $k(T)$. Converged quantum mechanical calculations of $N(E)$ remain a challenge even for three- and four-atom systems, and a longstanding goal of theoreticians has been to calculate $N(E)$ accurately and efficiently using semiclassical methods. In this article we present a variety of methods for achieving this goal, by combining semiclassical initial value propagation methods with a reactant–product wavepacket correlation function approach to reactive scattering. The correlation function approach, originally developed for transitions between asymptotic internal states of reactants and products, is here reformulated using wavepackets in an arbitrary basis, so that $N(E)$ can be calculated entirely from trajectory dynamics in the vicinity of the transition state. This is analogous to the approaches pioneered by Miller for the quantum calculation of $N(E)$, and leads to a reduction in the number of trajectories and the propagation time. Numerical examples are presented for both one-dimensional test problems and for the collinear hydrogen exchange reaction.

1 Introduction

Calculation of chemical reaction rates lies at the very core of theoretical chemistry, since they determine the relative significance of competing chemical processes. Reaction rates depend strongly, up to orders of magnitude, on the temperature of a reactive system; however, for a given energy E , the reaction probability is a universal quantity, independent of temperature. The reaction rate for any temperature may be obtained from the reaction probability by Boltzmann averaging over the energy E .

The reaction probability may be defined at different levels of detail. The most complete information about scattering is given by the S -matrix

$$S(E) = \{S_{\beta\alpha}(E)\} \quad (1)$$

where $|S_{\beta\alpha}(E)|^2$ is the probability of a transition from a specific state α of reactants to a specific state β of products to occur at total energy E . Often, however, only some state-averaged quantities are of interest, *e.g.* the initial (final) state selected *total* reaction probability

$$N_{\alpha(\beta)}(E) = \sum_{\beta(\alpha)} |S_{\beta\alpha}(E)|^2 \quad (2)$$

or the *cumulative* reaction probability

$$N(E) = \sum_{\alpha\beta} |S_{\beta\alpha}(E)|^2 \quad (3)$$

It is the cumulative reaction probability, averaged over the energy distribution, that gives the thermal reaction rate constant

$$k(T) = 2\pi\hbar Q(T)^{-1} \int_0^\infty N(E) \exp\left(-\frac{E}{kT}\right) dE \quad (4)$$

where $Q(T)$ is the reactant partition function.

From the practical point of view it is advantageous to find the state-averaged reaction probabilities directly without

explicit reference to the state-to-state probabilities. An example of such a formulation is the expression of Miller *et al.*¹

$$N(E) = \frac{(2\pi\hbar)^2}{2} \text{Tr}(\bar{F}\delta(E-H)\bar{F}\delta(E-H)) \quad (5)$$

where H is the Hamiltonian of a system and \bar{F} is the symmetrized flux operator. Formally, the trace form of $N(E)$ can be evaluated in any complete basis. Since eqn. (5) does not refer to the asymptotic states explicitly, $N(E)$ can be calculated from dynamics in the transition state region (*i.e.* interaction region) only. A variation on this formulation, which appears to be better suited for numerical work, is the transition state probability operator approach of Manthe, Miller and co-workers.^{2–4}

The time-dependent formulation of reactive scattering,^{5,6} where reagents are described in terms of square-integrable wavepackets, is conceptually simple, reflecting the temporal evolution of a reactive collision. In recent years, this approach has become a practical method for performing scattering calculations, as a result of advances in numerical methods for wavepacket propagation as well as the emergence of a variety of efficient methods for calculating reaction probabilities from the time-evolving wavepacket.^{7–10} Neuhauser *et al.* employed the flux operator to obtain state-to-state and total reaction probabilities.^{11–13} Introduction of an absorbing potential beyond the dividing surface where the flux was calculated allowed for a relatively small grid. This method has been used for a wide variety of systems, including the four-atom $\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$ reaction.^{14–18} Jäckle and Meyer have further extended the formalism of the reactive flux method in the presence of an absorbing potential.¹⁹ Light and Zhang have developed a quantum transition state wavepacket method, in which wavepackets are constructed as products of flux operator eigenfunctions and internal eigenfunctions along an arbitrary dividing surface.^{20–23} This method allows one to consider just the interaction region dynamics and to minimize the number of wavepackets, since for reactions with a barrier

the number of internal transition states is smaller than the number of internal asymptotic states.

There is another class of time-dependent approaches, based on the analysis of the time-correlation functions of wavepackets.^{24–28} These approaches have the advantages of low storage requirements and may be used in conjunction with high-resolution spectral methods.^{29–32} Among the time-correlation approaches, the formulation of Tannor and Weeks^{27,28} has the attractive feature of treating reactants and products symmetrically, and provides the flexibility to calculate the correlation function in the interaction region, rather than the asymptotic region, if so desired. In this paper we start with the wavepacket correlation formulation for the *S*-matrix elements of Tannor and Weeks^{27,28} and extend it to the calculation of the cumulative reaction probability, $N(E)$, with arbitrary internal functions. The wavepacket correlation expression of Garashchuk and Tannor for the *total* state-selected probability $N_\alpha(E)$ (ref. 33) is also generalized for direct calculation of $N(E)$. The projection operator used in the latter formalism is closely related to the flux operator, enabling us to establish the relationship between the current work and eqn. (5).

Despite all the conceptual advances and rapid growth of computer capabilities, the actual calculations remain a great challenge. To date, the largest systems for which full quantum-mechanical calculations of reaction probabilities have been performed are four-atom systems, $\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$ and $\text{H}_2 + \text{CN} \rightarrow \text{HCN} + \text{H}$ and their isotopic analogs. The numerical effort of the exact quantum-mechanical propagation grows exponentially with the size of the system. An appealing alternative to full quantum-mechanical calculations in chemical dynamics are semiclassical methods. Such methods combine the conceptual simplicity of classical mechanics with the ability to describe quantum phenomena. Semiclassical methods can provide considerable physical insight and may require less computational effort and have more favorable scaling with the size of a system than a full quantum calculation, a feature which is crucial for the treatment of multidimensional systems. A significant advantage of the new wavepacket correlation function expressions for $N(E)$ mentioned above is that they may be calculated conveniently using semiclassical mechanics. In this paper, we implement the expressions using the semiclassical propagator of Herman and Kluk (HK), which is emerging as the semiclassical method of choice for many problems of chemical interest.^{34–37}

The rest of the paper is organized as follows. Section 2 contains a few definitions from scattering theory, followed by a short derivation of Tannor and Weeks' expression for individual *S*-matrix element in terms of wavepacket cross-correlation functions. Section 3 derives an expression for the total state-selected reaction probability, $N_\alpha(E)$, in terms of the *auto*-correlation of a suitably projected wavepacket. This formula is then implemented semiclassically, and it is seen that the projection operator is surprisingly expensive to implement using classical trajectories. In Section 4, a generalization of the wavepacket correlation formalism for the cumulative reaction probability, $N(E)$, is presented. In contrast with the state-selected total reaction probability, the calculation of the cumulative reaction probability is quite efficient and robust when implemented semiclassically, as illustrated for the collinear hydrogen exchange reaction. To our knowledge, this is the first successful semiclassical calculation of $N(E)$ in more than one degree of freedom. Section 5 concludes.

2 The time-dependent wavepacket correlation approach to scattering

2.1 Some definitions from scattering theory

Consider the scattering of a reactive system with internal degrees of freedom.⁶ A Hamiltonian $H(R, r)$ governs the

dynamics of the system, where R is a translational coordinate and r is a set of internal coordinates. The reactant and product arrangement channels are labeled α and β respectively. A central assumption of scattering theory is that the interaction between the fragments vanishes when they are sufficiently far apart. This means that H can be written as the sum of an asymptotic Hamiltonian $H_{\alpha(\beta)}^0$, and an interaction potential $\lim_{R \rightarrow \infty} V_{\alpha(\beta)} = 0$, $H = H_{\alpha(\beta)}^0 + V_{\alpha(\beta)}$. For every value of the energy E in the continuum there are degenerate eigenfunctions of H , labeled as incoming (+) or outgoing (−), depending on the direction of the translation momentum relative to the interaction region:

$$H|\psi_{\alpha,E}^+\rangle = E|\psi_{\alpha,E}^+\rangle \quad \text{and} \quad H|\psi_{\beta,E}^-\rangle = E|\psi_{\beta,E}^-\rangle \quad (6)$$

The first set of energy eigenstates $\{|\psi_{\alpha,E}^+\rangle\}$ correlates (*i.e.* is equivalent in the asymptotic region) to the eigenstates of H_α^0 of the same energy E , with the same internal label α and incoming towards the interaction region from the reactant side. The second set $\{|\psi_{\beta,E}^-\rangle\}$ correlates with the eigenstate of H_β^0 of the same energy E and with the same internal label β , but outgoing from the interaction region to the product side. The parameter E is the total energy of the system. All energy eigenfunctions within both sets are mutually orthogonal

$$\begin{aligned} \langle \psi_{\alpha,E}^+ | \psi_{\alpha',E'}^+ \rangle &= \delta_{\alpha\alpha'} \delta(E - E') \quad \text{and} \\ \langle \psi_{\beta,E}^- | \psi_{\beta',E'}^- \rangle &= \delta_{\beta\beta'} \delta(E - E') \end{aligned} \quad (7)$$

The relation between these two sets is expressed through matrix elements

$$\langle \psi_{\beta,E}^- | \psi_{\alpha,E}^+ \rangle = S_{\beta\alpha}(E) \delta(E - E') \quad (8)$$

that form the *S*-matrix $\mathcal{S}(E) = \{S_{\beta\alpha}(E)\}$.

2.2 Expression for the *S*-matrix elements

In the time-dependent framework, the energy eigenfunctions $|\psi_{\alpha,E}^+\rangle$ and $|\psi_{\beta,E}^-\rangle$ can be obtained from the time evolution of wavepackets. These wavepackets are localized in space and spread in energy

$$\begin{aligned} |\Phi_\alpha^+\rangle &= \int_0^\infty \eta_\alpha(E) |\psi_{\alpha,E}^+\rangle dE \quad \text{and} \\ |\Phi_\beta^-\rangle &= \int_0^\infty \zeta_\beta(E) |\psi_{\beta,E}^-\rangle dE \end{aligned} \quad (9)$$

In the infinite past the reactant wavepacket $|\Phi_\alpha^+\rangle$ is located in the asymptotic region of the reactants. We require $|\Phi_\alpha^+\rangle$ to be a direct product of an incoming wavepacket in the translational degree of freedom and an eigenstate of the internal reactant Hamiltonian with quantum numbers α in the infinite past. The overall direction of motion of $|\Phi_\alpha^+\rangle$ in the translational coordinate is towards the interaction region. Similarly, the product wavepacket $|\Phi_\beta^-\rangle$ has to be in the asymptotic region of products in the infinite future, where it is separable and its internal state is described by a single set of internal quantum numbers β . This wavepacket is purely outgoing (*i.e.* it moves away from the interaction region when propagated forward in time under H_β^0). The wavepackets can be constructed in asymptotic regions of the potential[†] as

$$\begin{aligned} |\Phi_\alpha^+\rangle &= |g^+(R)\rangle \times |\chi_\alpha(r)\rangle \quad \text{and} \\ |\Phi_\beta^-\rangle &= |g^-(R)\rangle \times |\chi_\beta(r')\rangle \end{aligned} \quad (10)$$

The functions $g^+(R)$ and $g^-(R')$ are wavepackets in the translational coordinates, and the functions $\chi_\alpha(r)$ and $\chi_\beta(r')$ are eigenstates of the asymptotic internal Hamiltonians of reactants and products, $h_{\alpha(\beta)} |\chi_{\alpha(\beta)}\rangle = E_{\alpha(\beta)} |\chi_{\alpha(\beta)}\rangle$.

[†] The initial and final wavepackets can also be constructed in the interaction region of the potential using reactant and product Møller operators.

The Fourier transforms of $|\Phi_\alpha^+\rangle$ and $|\Phi_\beta^-\rangle$ as functions of time give the energy eigenfunctions

$$|\psi_{\alpha,E}^+\rangle = \frac{(2\pi)^{-1}}{\eta_\alpha(E)} \int_{-\infty}^{\infty} e^{-iHt} |\Phi_\alpha^+\rangle e^{iEt} dt \\ = \frac{1}{\eta_\alpha(E)} \delta(E - H) |\Phi_\alpha^+\rangle \quad (11)$$

and

$$|\psi_{\beta,E}^-\rangle = \frac{1}{\zeta_\beta(E)} \delta(E - H) |\Phi_\beta^-\rangle \quad (12)$$

where we have used the integral representation of the operator $\delta(E - H)$

$$\delta(E - H) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i(H-E)t} dt \quad (13)$$

We use $\hbar = 1$ throughout. The energy expansion coefficients $\eta_\alpha(E)$ and $\zeta_\beta(E)$ can be found analytically as an overlap of a wavepacket and an energy eigenstate of the asymptotic Hamiltonian.²⁷

Using eqns. (11) and (12), the definition of the S -matrix (8) becomes

$$S_{\beta\alpha}(E) \delta(E - E') \\ = \frac{1}{\zeta_\beta^*(E) \eta_\alpha(E)} \langle \Phi_\beta^- | \delta(E - H) \delta(E' - H) | \Phi_\alpha^+ \rangle \\ = \frac{1}{\zeta_\beta^*(E) \eta_\alpha(E)} \langle \Phi_\beta^- | \delta(E - H) | \Phi_\alpha^+ \rangle \delta(E - E') \quad (14)$$

Integrating this expression over E' and replacing $2\pi\delta(E - H)$ by the time integral (13), we obtain the S -matrix element as a function of energy E from the Fourier transform of the reactant/product wavepacket correlation function

$$S_{\beta\alpha}(E) = \frac{(2\pi)^{-1}}{\zeta_\beta^*(E) \eta_\alpha(E)} \int_{-\infty}^{\infty} \langle \Phi_\beta^- | e^{-iHt} | \Phi_\alpha^+ \rangle e^{iEt} dt \quad (15)$$

For derivations of the cumulative reaction probability in Section 4, it is essential to express the energy normalization functions $|\zeta_\beta(E)|$ and $|\eta_\alpha(E)|$ in terms of reactant/reactant and product/product wavepacket correlation functions. Using eqn. (11) and (7), we have

$$\langle \psi_{\alpha,E}^+ | \psi_{\alpha',E'}^+ \rangle = \frac{1}{\eta_\alpha^*(E) \eta_{\alpha'}(E')} \langle \Phi_\alpha^+ | \delta(E - H) \delta(E' - H) | \Phi_{\alpha'}^+ \rangle \\ = \frac{1}{|\eta_\alpha(E)|^2} \langle \Phi_\alpha^+ | \delta(E - H) | \Phi_\alpha^+ \rangle \delta(E - E') \\ = \delta(E - E') \delta_{\alpha\alpha'}$$

Removing the δ -function and using eqn. (13), we find the energy expansion coefficients for reactants

$$|\eta_\alpha(E)|^2 = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle \Phi_\alpha^+ | e^{-iHt} | \Phi_\alpha^+ \rangle e^{iEt} dt \quad (16)$$

and similarly for the products,

$$|\zeta_\beta(E)|^2 = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle \Phi_\beta^- | e^{-iHt} | \Phi_\beta^- \rangle e^{iEt} dt \quad (17)$$

Combining eqn. (15) with eqns. (16) and (17) we obtain

$$|S_{\beta\alpha}(E)|^2 = \frac{\left| \int_{-\infty}^{\infty} \langle \Phi_\beta^- | e^{-iHt} | \Phi_\alpha^+ \rangle e^{iEt} dt \right|^2}{\int_{-\infty}^{\infty} \langle \Phi_\beta^- | e^{-iHt} | \Phi_\beta^- \rangle e^{iEt} dt \int_{-\infty}^{\infty} \langle \Phi_\alpha^+ | e^{-iHt} | \Phi_\alpha^+ \rangle e^{iEt} dt} \quad (18)$$

Eqn. (15) and its equivalent, eqn. (18), are explicitly time reversible, and the time propagation can be partitioned

between reactants (forward in time) and products (back in time). A single calculation gives an element of the S -matrix (or a column, if the correlation functions for all product states are calculated simultaneously) for a range of energies that depends on the choice of reactant and product wavepackets. Note, that no additional wavepacket propagation is necessary to obtain the energy normalization factors given by eqn. (16) and (17), since they can be calculated at the same time as the cross-correlation function in the interaction region, provided both reactant and product wavepackets are propagated.

In this section, we were concerned with transition probabilities from individual asymptotic states of reactants to individual asymptotic states of products. As a result, we had to define our wavepackets in terms of eigenstates of the asymptotic internal Hamiltonians for reactants and products. However, the cumulative reaction probability, $N(E)$, since it depends only on the reactive dynamics in the interaction region, can in principle be determined without a knowledge of the asymptotic states. In Section 4, we generalize eqn. (18) to calculation of the cumulative reaction probability in an arbitrary internal state basis set.

3 Calculation of the initial state selected total reaction probability using projected-wavepacket autocorrelation functions

3.1 Wavepacket correlation expression

The goal of this section is to calculate reaction probabilities averaged over the final (or initial) distribution of internal states,

$$N_{\alpha(\beta)}(E) = \sum_{\beta(\alpha)} |S_{\beta\alpha}(E)|^2$$

This quantity does not necessarily require the knowledge of the product (or reactant) asymptotic internal eigenstates or the dynamics in the exit (or entrance) region of the potential, where the distribution between the internal eigenstates of fragments is still changing but the total reaction probability has converged. In this section we take advantage of this idea to develop a variety of simple expressions for $N_{\alpha(\beta)}(E)$ which are in the spirit of the wavepacket correlation function approach of the previous section but do not require information on the asymptotic product (or reactant) asymptotic internal states, or the exit (entrance) channel dynamics.

The starting point of the derivations is the definition of the S -matrix:

$$S_{\beta\alpha}(E) \delta(E - E') = \langle \psi_{\beta,E'}^- | \psi_{\alpha,E}^+ \rangle \quad (19)$$

The reaction probability from the initial state with internal quantum numbers α to a specific final state of the reactants with the internal quantum numbers β is proportional to

$$S_{\beta\alpha}^*(E) \delta(E - E') S_{\beta\alpha}(E'') \delta(E' - E'') \\ = \langle \psi_{\alpha,E}^+ | \psi_{\beta,E'}^- \rangle \langle \psi_{\beta,E'}^- | \psi_{\alpha,E''}^+ \rangle \quad (20)$$

Integration over E' and summation over all β of the product channel gives

$$\sum_{\beta} S_{\beta\alpha}^*(E) S_{\beta\alpha}(E'') \delta(E - E'') = \langle \psi_{\alpha,E}^+ | \hat{P}^+ | \psi_{\alpha,E''}^+ \rangle \quad (21)$$

where \hat{P}^+ denotes the operator projecting onto products

$$\hat{P}^+ \equiv \sum_{\beta} \int_0^{\infty} |\psi_{\beta,E'}^- \rangle \langle \psi_{\beta,E'}^- | dE' \quad (22)$$

Substituting eqn. (11), which relates the energy eigenfunctions to the time evolution of wavepackets, into eqn. (21), and using the commutativity of the projection operator \hat{P}^+

and the Hamiltonian H , we have

$$\begin{aligned} \sum_{\beta} S_{\beta\alpha}^*(E) S_{\beta\alpha}(E'') \delta(E - E'') \\ = \frac{(2\pi)^{-2}}{\eta_{\alpha}^*(E) \eta_{\alpha}(E'')} \langle \Phi_{\alpha}^+ | \delta(E - H) \hat{P}^+ \delta(E'' - H) | \Phi_{\alpha}^+ \rangle \\ = \frac{(2\pi)^{-2}}{\eta_{\alpha}^*(E) \eta_{\alpha}(E'')} \langle \Phi_{\alpha}^+ | \delta(E - H) \hat{P}^+ | \Phi_{\alpha}^+ \rangle \delta(E'' - E) \quad (23) \end{aligned}$$

Integrating eqn. (23) over E'' and replacing $\delta(E - H)$ by its integral expression eqn. (13), as before, we obtain

$$N_{\alpha}(E) = \frac{(2\pi)^{-1}}{|\eta_{\alpha}(E)|^2} \int_{-\infty}^{\infty} dt \langle \Phi_{\alpha}^+ | \hat{P}^+ e^{-iHt} | \Phi_{\alpha}^+ \rangle e^{iEt} \quad (24)$$

Eqn. (24) expresses $N_{\alpha}(E)$ as the cross-correlation function of the incoming wavepacket $|\Phi_{\alpha}\rangle$ with its reactive part $\hat{P}^+ |\Phi_{\alpha}\rangle$.

Using the properties of the projection operator $(\hat{P}^+)^2 = \hat{P}^+$ and $(\hat{P}^+)^{\dagger} = \hat{P}^+$, and the energy normalization, eqn. (16), we can rewrite eqn. (24) in a symmetrized way

$$N_{\alpha}(E) = \frac{\int_{-\infty}^{\infty} dt \langle \hat{P}^+ \Phi_{\alpha}^+ | e^{-iHt} | \hat{P}^+ \Phi_{\alpha}^+ \rangle e^{iEt}}{\int_{-\infty}^{\infty} dt \langle \Phi_{\alpha}^+ | e^{-iHt} | \Phi_{\alpha}^+ \rangle e^{iEt}} \quad (25)$$

This expression is manifestly real since it involves the Fourier transform of the autocorrelation function. It expresses the state-selected total reaction probability as a ratio of two spectra, that of the reactive wavepacket divided by that of the initial wavepacket, which has both reactive and non-reactive components. The latter spectrum normalizes the former, ensuring that the total reaction probability is between 0 to 1 and that the result at each energy is independent of the choice of energy distribution in the initial translational wavepacket.‡

3.2 Numerical implementation: scattering on the Eckart barrier using the semiclassical propagator of Herman and Kluk

To implement eqns. (24) and (25) it is convenient to use an alternative expression for the projection operator, defined by eqn. (22),

$$\hat{P}^+ = \lim_{t \rightarrow \infty} e^{iHt} h(s) e^{-iHt} \quad (26)$$

The reaction coordinate s is $+\infty$ in the asymptotic region of products and it is $-\infty$ in the asymptotic region of reactants. The Heaviside function,

$$h(s) = \begin{cases} 1 & \text{if } s > 0 \\ 0 & \text{if } s < 0 \end{cases} \quad (27)$$

performs the projection of a wavefunction onto products in the infinite future.

Thus, quantum-mechanical implementation of eqns. (24) and (25) is straightforward. As a first step, the wavepacket $|\Phi_{\alpha}\rangle$ is propagated forward in time. Its autocorrelation function is calculated during this propagation if necessary. The propagation is stopped at time T , when the norm of the wavefunction in the product region becomes constant. Generally, it happens before the wavepacket reaches the asymptotic region, while transitions between different internal states of products still take place. The non-reactive part of a wavepacket is discarded

$$\hat{P}^+ \Phi_{\alpha}^+(s, T) = h(s) \Phi_{\alpha}^+(s, T)$$

‡ All expressions for the state-selected total reaction probability can be reversed to treat the case of a single well-defined internal state of products, summed over all internal states of reactants. To do so, the labels α and β must be interchanged, and the projection operator must be redefined to project onto reactants.

The reactive part is propagated further, and its autocorrelation

$$C(t) = \langle \hat{P}^+ \Phi_{\alpha}^+(T) | \hat{P}^+ \Phi_{\alpha}^+(T + t) \rangle$$

is computed.

Propagation just forward or just backward in time is sufficient, since $C(-t) = C^*(t)$. Moreover, using eqn. (24), one can calculate the correlation function of the projected wavefunction and the initial wavepacket

$$C(T + t) = \langle \Phi_{\alpha}^+(0) | \hat{P}^+ \Phi_{\alpha}^+(T + t) \rangle$$

for times $t = [T, 0]$. This correlation function $C(t)$ also satisfies the property $C(-t) = C^*(t)$, since eqns. (24) and (25) are equivalent. Fig. 1 illustrates this procedure for scattering on a barrier in one dimension.

We have implemented eqns. (24) and (25) semiclassically on a one-dimensional problem—scattering from the Eckart barrier. The semiclassical application, using the propagator of Herman and Kluk (HK), was more challenging than we expected, but revealed interesting details about the propagator. The semiclassical propagator is described in Appendix A. The Hamiltonian of the system is

$$H = \frac{p^2}{2} + \frac{D}{\cosh(\lambda s)^2}$$

with parameter values being $D = 16.0$ and $\lambda = 1.1243$. The initial wavepacket has the Gaussian form

$$\Phi^+(s, 0) = \left(\frac{\gamma}{\pi}\right)^{1/4} \exp\left(-\frac{\gamma}{2}(s - s_0)^2 + ip_0(s - s_0)\right) \quad (28)$$

with $\gamma/2 = 6.0$, $s_0 = 3.5$, $p_0 = 6.0$.

Since the HK propagator is a superposition of the contributions from classical trajectories, the correlation function is also a sum over the trajectories

$$\begin{aligned} C^{sc}(t) &= \int \int ds' ds'' \Phi^{+*}(s', 0) K^{sc}(s', t; s'', 0) \Phi^+(s'', 0) \\ &= \sum_{qp} C_{qp}(t) \end{aligned}$$

It seemed natural, in the context of semiclassical propagation, to try to replace the quantum projection operator pro-

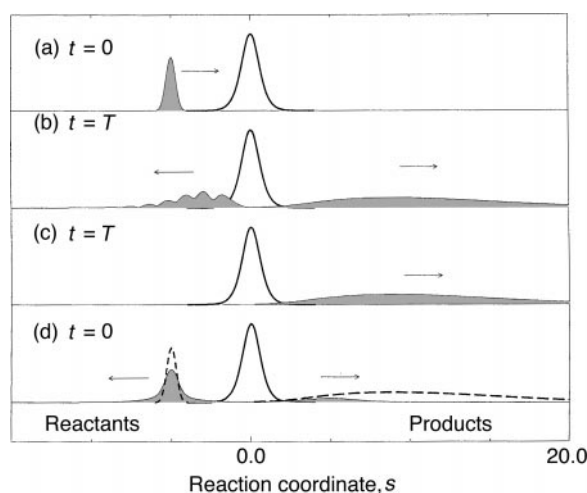


Fig. 1 Scattering on a one-dimensional barrier: (a) at $t = 0$ an initial wavepacket $|\Phi(0)\rangle$ (shaded) starts moving towards the barrier (— on all panels); (b) at time $t = T$ the wavepacket $|\Phi(T)\rangle$ (shaded) is split into two parts, the reactive part is on the right-hand side of the barrier and the non-reactive part is on the left-hand side; (c) the non-reactive part of the wavepacket is discarded when the transmission of the amplitude towards the product region has stopped, $\hat{P}|\Phi(T)\rangle$; (d) the reactive part of the wavepacket $|\hat{P}\Phi(T)\rangle$ (shaded) is propagated back in time from $t = T$ to $t = 0$ and its autocorrelation $\langle \hat{P}\Phi(T) | \hat{P}\Phi(T - t) \rangle$ (— = $|\hat{P}\Phi(T)\rangle$) or the correlation with the initial wavepacket (---) $\langle \Phi(0) | \hat{P}\Phi(T - t) \rangle$ is computed.

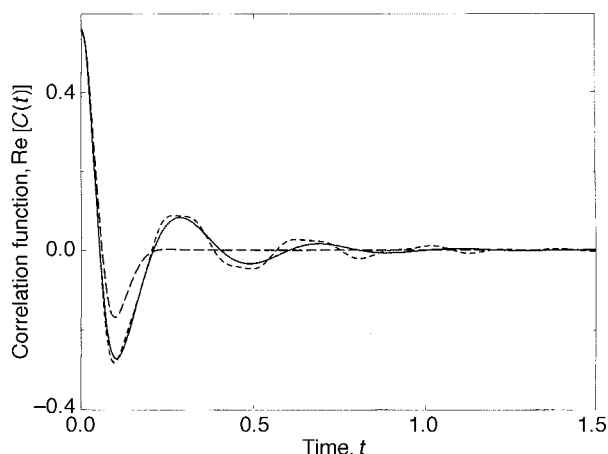


Fig. 2 Autocorrelation function $C(t)$ of the projected wavefunction for the Eckart barrier, obtained semiclassically with the Herman-Kluk propagator (---), semiclassically with the classical reactivity criterion (— · —) and quantum-mechanically (—). The real part of $C(t)$ is plotted.

cedure by a classical reactivity criterion, in which the contribution of reactive trajectories to the correlation function is kept, and that of non-reactive trajectories is discarded, *i.e.*

$$C^{cl}(t) = \langle \Phi^+(0) | \hat{P}^{+cl} \Phi^+(t) \rangle = \sum_{qp} C_{qpt} \theta_{qp} \quad (29)$$

with θ_{qp} defined as

$$\theta_{qp} = \begin{cases} 1 & \text{if } q(q_i, p_i, t \rightarrow -\infty) < 0 \\ & \text{and } q(q_i, p_i, t \rightarrow \infty) > 0 \\ 0 & \text{if } q(q_i, p_i, t \rightarrow -\infty) < 0 \\ & \text{and } q(q_i, p_i, t \rightarrow \infty) < 0 \end{cases} \quad (30)$$

For the one-dimensional case this criterion is equivalent to keeping only trajectories started from the reactant side with momentum towards the barrier and with energy greater than the barrier top. We tested this idea in eqn. (24) for the scattering on the Eckart barrier. Unfortunately, the agreement with the quantum results was poor (Fig. 2). The classical reactivity criterion is applicable only when the reactive and non-reactive trajectories become spatially separated. For earlier times the interference between trajectories is crucial and classically reactive trajectories do not adequately describe the semiclassical reactive wavefunction. We found that to obtain satisfactory accuracy we had to reexpand the propagated-projected wavefunction at the “infinite future” in a new set of

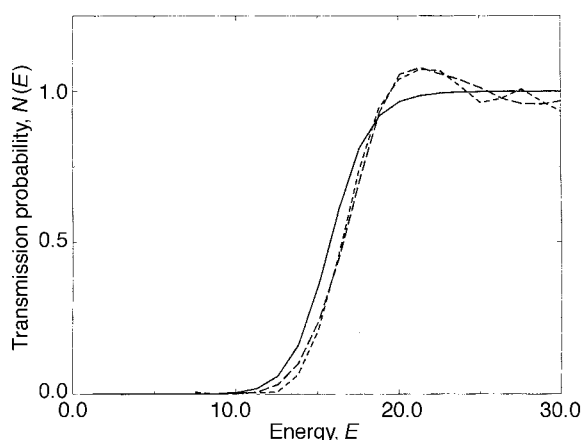


Fig. 3 Transmission probability $N(E)$ for the Eckart barrier, obtained semiclassically using eqn. (24) with one projection operator \hat{P} (---), using eqn. (25) with two projection operators \hat{P}^2 (— · —), and the analytical results (—).

trajectories and propagate it back in time, calculating the overlap with the initial reactant wavefunction. The new set of trajectories covered a much larger section of the phase space, since the wavefunction in the infinite future is spread. The reexpansion weighting coefficients for every new trajectory were calculated once at $t = T$. An alternative is to calculate the autocorrelation function shifted in time by T , where the initial set of reactive trajectories can be reused, but summation over two sets of trajectories needs to be performed at every time step to compute $C^{sc}(t)$. The explicit expression for the semiclassical propagator, eqn. (A1), combined with the expression for the initial wavefunction, eqn. (28), gives

$$\begin{aligned} C^{sc}(t) &= \langle \hat{P}^+ \Phi_\alpha^+(T) | \hat{P}^+ \Phi_\alpha^+(T+t) \rangle \\ &= \frac{1}{2\pi} \sum_{uvqp} e^{i(S_{uvT} - S_{qpT})} R_{qpT}^* R_{uvT} \theta_{qp} \theta_{uv} \\ &\quad \times f(q_i, p_i, s_0, p_0) f(u_i, v_i, q_T, p_T) f^*(u_t, v_t, q_T, p_T) \end{aligned} \quad (31)$$

where

$$\begin{aligned} f(q, p, u, v) &= \exp\left(-\frac{\gamma}{4}(q-u)^2 - \frac{1}{4\gamma}(p-v)^2\right. \\ &\quad \left.+ \frac{i}{2}(q-u)(p+v)\right) \end{aligned}$$

In practice, this means that a set of trajectories $\{q_i, p_i\}$ sampling the initial wavepacket $\Phi_\alpha^+(0)$ is propagated until time T , when the bifurcation of the wavepacket is complete; at this point all the information about the trajectories at time T is stored. Now the trajectories $\{q_T, p_T\}$ are relabeled as $\{u_i, v_i\}$ and propagated further forward in time. Since in eqn. (31) we propagate both bra and ket up to time T we have two summations over the set $\{q, p\}$, one describing the stationary wavepacket $\Phi(T)$, and the other over the set $\{u, v\}$, describing the further evolution of $\Phi(T+t)$ in time. Owing to the Heaviside functions, the nonzero contribution comes only from the reactive trajectories. At time T the bifurcation is already complete and there can be no interference between reactive and non-reactive trajectories. Thus, we can use just θ_{qp} or θ_{uv} in eqn. (31) instead of their product. This is equivalent to the statement that after time T the property $(\hat{P}^+)^2 = \hat{P}^+$ is fulfilled. Semiclassically, propagation forward in time into the asymptotic region is convenient since there is no concern about the grid size and the propagation is simpler in the asymptotic region. Here we used 1000 classical trajectories, equally spaced in position q and distributed in momentum p as $p^2 = 2V_0 + p_0^2$ with equally spaced p_0 . The semiclassical correlation function is shown in Fig. 2. The semiclassical transmission probability is shown in Fig. 3 and compared with the analytical result.

The two semiclassical (HK) calculations give $N(E)$ of similar accuracy, capturing the correct general picture but underestimating tunneling and deviating slightly from unity in the high energy region, which is consistent with the S -matrix calculation reported earlier.²⁷

We can conclude that for the HK propagator a semiclassical criterion for the reactive wavefunction, keeping only the contribution from classically reactive trajectories, cannot be substituted for the quantum projection operator on the wavefunction. The rigorous projection procedure requires calculating cross overlaps of a large number of Gaussians at every time step or sampling of a projected wavefunction, which is quite spread, with new trajectories. Both alternatives are computationally inefficient and prohibitively expensive in more than one dimension. The peculiar result is that all the semiclassical $N(E)$ s are of the same quality, and that the HK propagator is conceptually closer to a quantum-mechanical, rather than to a classical propagator.

4 Cumulative reaction probabilities using wavepacket correlation functions with an arbitrary internal basis

The derivations of Sections 2 and 3 for state-to-state and initial-state-selected total reaction probabilities involve energy eigenstates and wavepackets with well defined internal quantum numbers α for reactants and/or β for products. In this section, expressions for $|S_{\beta\alpha}(E)|^2$ and $N_\alpha(E)$ in terms of wavepacket correlation functions are generalized for calculation of the cumulative reaction probability with an arbitrary complete set of internal functions.

4.1 $N(E)$ based on the reactant/product wavepacket time-correlation functions

Note that to obtain the cumulative reaction probability as a sum of the state-to-state probabilities one has to define and propagate several wavepackets. The number of the wavepackets is equal to the number of the internal states. Thus, for a system with $N + 1$ internal eigenstates in the asymptotic channels of products and reactants, one needs a set $\{\Phi_r\}$ of $N + 1$ wavepackets on the reactant side, that correlate with the internal eigenstates of reactants and a set of $N + 1$ wavepackets $\{\Phi_p\}$ on the product side, correlating with internal product eigenstates. Now, let us consider wavepackets that are arbitrary in the internal degrees of freedom, instead of being the eigenstates. These wavepackets are some unknown linear combinations of the energy eigenstates with different internal quantum number, $\{|\psi_{\alpha,E}^+\rangle\}$ with incoming boundary conditions for reactant wavepackets

$$\begin{cases} |\Phi_r^0\rangle = \int_0^\infty (\eta_{00}(E)|\psi_{0,E}^+\rangle + \cdots + \eta_{0N}(E)|\psi_{N,E}^+\rangle) dE \\ \vdots \\ |\Phi_r^N\rangle = \int_0^\infty (\eta_{N0}(E)|\psi_{0,E}^+\rangle + \cdots + \eta_{NN}(E)|\psi_{N,E}^+\rangle) dE \end{cases} \quad (32)$$

and $\{|\psi_{\beta,E}^-\rangle\}$ with outgoing conditions for product wavepackets

$$\begin{cases} |\Phi_p^0\rangle = \int_0^\infty (\zeta_{00}(E)|\psi_{0,E}^-\rangle + \cdots + \zeta_{0N}(E)|\psi_{N,E}^-\rangle) dE \\ \vdots \\ |\Phi_p^N\rangle = \int_0^\infty (\zeta_{N0}(E)|\psi_{0,E}^-\rangle + \cdots + \zeta_{NN}(E)|\psi_{N,E}^-\rangle) dE \end{cases} \quad (33)$$

The energy expansion coefficients can be arranged into matrices, that functions of the energy, where the first index, $i = 0, \dots, N$, labels wavepackets and the second index, $\alpha/\beta = 0, \dots, N$, labels energy eigenfunctions,

$$\mathbf{M}_r(E) = \{\eta_{i\alpha}(E)\} \quad (34)$$

and

$$\mathbf{M}_p(E) = \{\zeta_{i\beta}(E)\} \quad (35)$$

Thus, eqns. (32) and (33) can be rewritten as

$$(|\Phi_r^0\rangle \dots |\Phi_r^N\rangle) = \int_0^\infty dE (|\psi_{0,E}^+\rangle \dots |\psi_{N,E}^+\rangle) \mathbf{M}_r(E) \quad (36)$$

for reactants and

$$(|\Phi_p^0\rangle \dots |\Phi_p^N\rangle) = \int_0^\infty dE (|\psi_{0,E}^-\rangle \dots |\psi_{N,E}^-\rangle) \mathbf{M}_p(E) \quad (37)$$

for products. We emphasize that, the matrices $\mathbf{M}_{r/p}$ are unknown and will not appear in our final working expression. Here and below we decided to write vectors explicitly to avoid additional indices required for tensor notation.

We now propagate the reactant wavepackets and calculate all the correlation functions $C_r^{ij}(t) = \langle \Phi_r^i | \exp(-iHt) | \Phi_r^j \rangle$ for $\{i, j\} = 0 \dots N$. This defines an $(N + 1) \times (N + 1)$ matrix. The Fourier transforms of each element, $A_r^{ij}(E) = \int_{-\infty}^\infty dt C_r^{ij}(t) e^{iEt}$, form a new matrix, $\mathbf{A}_r(E)$. It is readily verified that $\mathbf{A}_r(E)$ may be written as

$$\begin{aligned} \mathbf{A}_r(E) &= 2\pi \int_0^\infty dE' \mathbf{M}_r^\dagger(E') \begin{pmatrix} \langle \psi_{0,E'}^+ | \\ \vdots \\ \langle \psi_{N,E'}^+ | \end{pmatrix} \delta(E - H) \\ &\times \int_0^\infty dE'' (|\psi_{0,E''}^+\rangle \dots |\psi_{N,E''}^+\rangle) \mathbf{M}_r(E'') \\ &= 2\pi \int_0^\infty dE' \int_0^\infty dE'' \mathbf{M}_r^\dagger(E') \\ &\times \delta(E' - E'') \delta(E - E'') \mathbf{M}_r(E'') \\ &= 2\pi \mathbf{M}_r^\dagger(E) \mathbf{M}_r(E) \end{aligned} \quad (38)$$

where $\delta(E' - E'')$ comes from the orthogonality of energy eigenstates at different energies. Similarly, we define the product/product correlation functions $C_p^{ij}(t) = \langle \Phi_p^i | \exp(-iHt) | \Phi_p^j \rangle$ and their Fourier transforms $A_p^{ij}(E)$. Following a derivation analogous to that for reactants, the Fourier transforms of the product/product correlation functions may be written in matrix form as

$$\mathbf{A}_p(E) = 2\pi \mathbf{M}_p^\dagger(E) \mathbf{M}_p(E) \quad (39)$$

Eqns. (38) and (39) provide a strategy for eliminating the unknown coefficients $\mathbf{M}_r(E)$ and $\mathbf{M}_p(E)$ in terms of the known matrices $\mathbf{A}_r(E)$ and $\mathbf{A}_p(E)$, provided that the matrix $\mathbf{M}_{r/p}$ and its adjoint always come together; below we will show that this is indeed the case.

Finally, we define the reactant/product correlation functions $C_{pr}^{ij}(t) = \langle \Phi_p^i | \exp(-iHt) | \Phi_r^j \rangle$ for $\{i, j\} = 0 \dots N$ and their Fourier transforms $A_{pr}^{ij}(E)$. Using eqns. (32) and (33), the matrix $\mathbf{A}_{pr}(E) = \{A_{pr}^{ij}(E)\}$ is

$$\begin{aligned} \mathbf{A}_{pr}(E) &= 2\pi \int_0^\infty dE' \mathbf{M}_p^\dagger(E') \begin{pmatrix} \langle \psi_{0,E'}^- | \\ \vdots \\ \langle \psi_{N,E'}^- | \end{pmatrix} \delta(E - H) \\ &\times \int_0^\infty dE'' (|\psi_{0,E''}^+\rangle \dots |\psi_{N,E''}^+\rangle) \mathbf{M}_r(E'') \\ &= 2\pi \int_0^\infty dE' \int_0^\infty dE'' \mathbf{M}_p^\dagger(E') \delta(E' - E'') \\ &\times \mathbf{S}_{rp}(E) \delta(E - E'') \mathbf{M}_r(E'') \\ &= 2\pi \mathbf{M}_p^\dagger(E) \mathbf{S}_{rp}(E) \mathbf{M}_r(E) \end{aligned} \quad (40)$$

where $\mathbf{S}_{rp}(E)$ is by definition the scattering matrix. More precisely, $\mathbf{S}_{rp}(E)$ is a part of the scattering matrix that describes chosen reactants and products. Note that the product of the state vectors of eqn. (40) produces the matrix $\mathbf{S}_{rp}(E)$ of dimension $(N + 1) \times (N + 1)$. Formally, if there exists an inverse of the matrices \mathbf{M}_r and \mathbf{M}_p , the S -matrix may be written as

$$\mathbf{S}_{rp}(E) = (2\pi)^{-1} \mathbf{M}_p^{-1}(E) \mathbf{A}_{pr}(E) \mathbf{M}_r^{-1}(E) \quad (41)$$

Now, realizing that the cumulative reaction probability can be expressed as a trace

$$N(E) = \text{Tr}(\mathbf{S}_{rp}(E) \mathbf{S}_{rp}^\dagger(E)) \quad (42)$$

§ The derivation can be easily modified for a system where the number of internal states for reactants and products are different.

and using eqn. (41) for the S -matrix, we can write

$$N(E) = \text{Tr}(\mathbf{M}_p^{\dagger-1}(E)\mathbf{A}_{pr}(E)\mathbf{M}_r^{-1}(E) \times \mathbf{M}_r^{\dagger-1}(E)\mathbf{A}_{pr}^{\dagger}(E)\mathbf{M}_p^{-1}(E)) \quad (43)$$

Permutating matrices inside the trace and using eqns. (38) and (39), we obtain

$$N(E) = \text{Tr}(\mathbf{A}_{pr}(E)\mathbf{A}_r^{-1}(E)\mathbf{A}_{pr}^{\dagger}(E)\mathbf{A}_p^{-1}(E)) \quad (44)$$

This is our final expression for $N(E)$ in terms of the dynamics of incoming and outgoing wavepackets in an arbitrary basis of internal functions. Note that all dependence on the matrices \mathbf{M}_r and \mathbf{M}_p , which would require knowledge of the asymptotic states, has disappeared.

If the wavepackets are initially located in the asymptotic region of the potential and they each correspond to a single internal eigenstate α and β , then eqn. (44) reduces to $N(E) = \sum_{\alpha\beta} |S_{\beta\alpha}(E)|^2$. Each S -matrix element in this sum takes the form of eqn. (18).

4.2 $N(E)$ based on the time-correlation of the wavepackets and the projection operator for products

To generalize eqn. (25) for the calculation of the initial state-selected reaction probability in the arbitrary internal basis, we take a set of $N + 1$ incoming wavepackets, $\{\Phi_r\}$ to span a space of $N + 1$ internal states given by eqn. (32). The matrix of Fourier transforms of all time-dependent correlation functions, which normalizes the energy eigenstates, is given by eqn. (38); i.e. $\mathbf{A}_r(E) = 2\pi\mathbf{M}_r^{\dagger}(E)\mathbf{M}_r(E)$. As before, we assume that \mathbf{M}_r is unknown but \mathbf{A}_r is readily computed. We define the matrix of Fourier transforms of the correlation functions of the projected wavepackets with the initial wavepackets as

$$\mathbf{A}_{\text{proj}}(E) = 2\pi \begin{pmatrix} \langle \Phi_r^0 | \\ \vdots \\ \langle \Phi_r^N | \end{pmatrix} \delta(E - H) \hat{P}^+ (| \Phi_r^0 \rangle \dots | \Phi_r^N \rangle) \quad (45)$$

where \hat{P}^+ is defined by eqn. (22). Note that eqn. (45) contains an outer product of a column and a row, generating a matrix.

The projection operator, eqn. (22), acts on the reactant wavepackets, eqn. (34), yielding

$$\begin{aligned} & \hat{P}_p(| \Phi_r^0 \rangle \dots | \Phi_r^N \rangle) \\ &= \int_0^\infty dE' (| \psi_{0,E'}^- \rangle \dots | \psi_{N,E'}^- \rangle) \begin{pmatrix} \langle \psi_{0,E'}^- | \\ \vdots \\ \langle \psi_{N,E'}^- | \end{pmatrix} \\ & \times \int_0^\infty dE (| \psi_{0,E}^+ \rangle \dots | \psi_{N,E}^+ \rangle) \mathbf{M}_r(E) \\ &= \int_0^\infty dE' \int_0^\infty dE (| \psi_{0,E'}^- \rangle \dots | \psi_{N,E'}^- \rangle) \\ & \times \mathbf{S}_{rp}(E) \delta(E - E') \mathbf{M}_r(E) \\ &= \int_0^\infty dE (| \psi_{0,E}^- \rangle \dots | \psi_{N,E}^- \rangle) \mathbf{S}_{rp}(E) \mathbf{M}_r(E) \end{aligned} \quad (46)$$

where we have used the definition of the S -matrix in eqn. (8). Substituting this result into eqn. (45) we obtain

$$\begin{aligned} \mathbf{A}_{\text{proj}}(E) &= 2\pi \int_0^\infty dE' \mathbf{M}_r^{\dagger}(E') \begin{pmatrix} \langle \psi_{0,E'}^+ | \\ \vdots \\ \langle \psi_{N,E'}^+ | \end{pmatrix} \\ & \times \delta(E - H) \int_0^\infty dE'' (| \psi_{0,E''}^- \rangle \dots | \psi_{N,E''}^- \rangle) \\ & \times \mathbf{S}_{rp}(E'') \mathbf{M}_r(E'') \\ &= 2\pi \mathbf{M}_r^{\dagger}(E) \mathbf{S}_{rp}^{\dagger}(E) \mathbf{S}_{rp}(E) \mathbf{M}_r(E) \end{aligned} \quad (47)$$

In the expression above, the product of the column $\{\langle \psi_{\alpha,E'}^+ | \}$ by the row $\{| \psi_{\beta,E''}^- \rangle\}$ gave the matrix $\mathbf{S}_{rp}^{\dagger}(E')\delta(E' - E'')$ according to eqn. (8).

Inverting the expression, taking a trace and permutating matrices inside the trace, we arrive at

$$\begin{aligned} N(E) &= \text{Tr}(\mathbf{S}_{rp}^{\dagger}(E) \mathbf{S}_{rp}(E)) \\ &= \text{Tr}(\mathbf{M}_r^{\dagger-1}(E) \mathbf{A}_{\text{proj}}(E) \mathbf{M}_r^{-1}(E)) \\ &= \text{Tr}(\mathbf{A}_{\text{proj}}(E) \mathbf{A}_r^{-1}(E)) \end{aligned} \quad (48)$$

Thus, we can evaluate $N(E)$ by propagating a set of incoming, otherwise arbitrary, wavepackets, projecting onto products and calculating correlation functions of these projected packets. As in Section 4.1, on the basis of asymptotic internal energy eigenstates eqn. (48) reduces to $N(E) = \sum_{\alpha} N_{\alpha}(E)$ with each term being of the form of eqn. (25).

4.3 Semiclassical implementation for the collinear $\text{H}_2 + \text{H}$ reaction

Here we implement eqn. (44), using the semiclassical propagator of Herman and Kluk, described in detail in Appendix A. The Wall-Porter potential is used as in ref. 34 for the semiclassical calculation of state-to-state probabilities. Reactant wavepackets $\{\Phi_r\}$ were set up in the Jacobi coordinates, $\{R, r\}$, as a direct product of the vibrational eigenstates and a Gaussian in the translational coordinate R

$$\begin{aligned} \Phi_r^n(R, r) &= \left(\frac{2\alpha}{\pi}\right)^{1/4} \exp(-\alpha(R - R_0)^2 \\ & \quad + ip_0(R - R_0)) \times \chi_n(r) \end{aligned} \quad (49)$$

The wavepackets $\{\Phi_p\}$ were set up in the product Jacobi coordinates and have the same parameters as the reactant wavepackets, except for the sign of the translational momentum to make them outgoing

$$\begin{aligned} \Phi_p^n(R', r') &= \left(\frac{2\alpha}{\pi}\right)^{1/4} \exp(-\alpha(R' - R_0)^2 \\ & \quad - ip_0(R' - R_0)) \times \chi_n(r') \end{aligned} \quad (50)$$

The parameters of the translational Gaussians were $\alpha = 4.5$, $q_0 = 4.7$ and $p_0 = -7.0$, and the internal functions are the eigenstates of the harmonic oscillator $V_h(r) = D(r - r_0)^2$, $D = 0.1898$ and $r_0 = 1.40083$ in atomic units, approximating the potential in the asymptotic region.

The reactant wavepackets were propagated up to time $T = 2760$ au with the time step $dt = 4.6$ au, and their time-dependent overlaps with the stationary product wavepackets were Fourier transformed. The reactant/reactant correlation functions of time duration 918 au were used to obtain the appropriate normalization in energy. They were almost identical to the quantum-mechanical results. The cumulative reaction probability for the HK and quantum-mechanical propagation is plotted in Fig. 4.

The agreement between the semiclassical $N(E)$ and the quantum-mechanical results is better than that obtained for the individual S -matrix elements in ref. 33. Here we used 10^6 classical trajectories, but 10 times fewer trajectories also gave semiquantitative agreement, although the discrepancies around the resonant and threshold energies were more pronounced. The matrix inversion in eqn. (44) did not pose a problem, since the reactant/reactant correlation functions are nonzero for the first half of the propagation time, and this is the time when semiclassical approximation works best.

The presence of resonances in the $\text{H} + \text{H}_2$ system and the constricted geometry make the state-to-state reaction probabilities quite structured and difficult to capture semiclassically. The direct calculation of the cumulative reaction

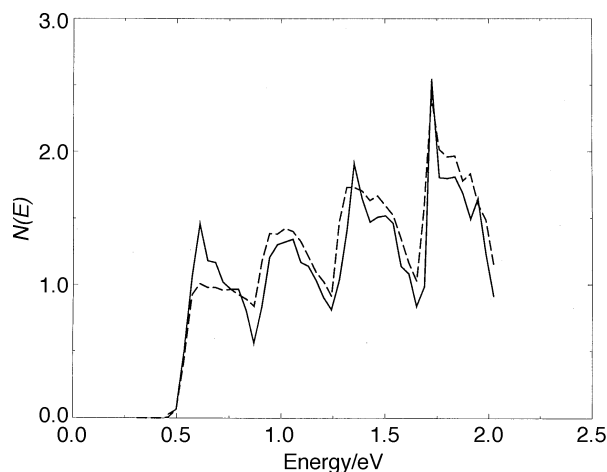


Fig. 4 The cumulative reaction probability, obtained from the semiclassical propagation of wavepackets (—) and the quantum-mechanical result (---). The wavepackets were initially located at $R_0 = 4.7$ au in the translational coordinate and were constructed as the harmonic oscillator eigenstates in vibrational coordinate.

probability is an easier task than obtaining all of the state-to-state probabilities. The analytical form of the overlap integrals $\langle g_s(0) | \Phi_r^n \rangle$ and $\langle \Phi_r^n | g_p(t) \rangle$ for the harmonic oscillator eigenstates with the HK Gaussians made the calculation several times faster. The width of the expansion Gaussians was taken to be $\gamma/2 = \alpha = 4.5$ au in both directions. The sampling in both the vibrational and translational coordinates was Gaussian. A single set of classical trajectories contributed to all correlation functions. The net result of all these simplifications was that the computer time for the exact quantum-mechanical and the semiclassical calculations was comparable.

5 Conclusion

Calculation of reaction probabilities is a fundamental problem of theoretical chemistry. In recent years, increasing computer power, progress in wavepacket time propagation methods and new formalisms have enabled researchers to solve the quantum scattering problem for small, 3–4 atom, systems. However, the prospect of the full quantum-mechanical solution for large systems is unlikely owing to the exponential scaling of numerical effort with the size of the system. Therefore, there is a great interest in developing alternative ways to treat reactive scattering. In this work we have addressed two issues—the development of new formulations for reactive scattering and the application of semiclassical methods to reactive systems.

The wavepacket correlation approach to reactive scattering has many attractive features from the computational and conceptual point of view. It yields the reaction probability for a range of energies from a single calculation, it requires negligible storage and only a single Fourier transform, and it allows for propagation of both reactant and product asymptotic states into the interaction region, thus reducing the grid size and improving accuracy.

Starting with the wavepacket correlation function expression for the state-to-state reaction probability of Tannor and Weeks, we developed a formulation for the state-selected total reaction probability using a projection operator in a time-dependent context. The relationship with the well-established trace formula of Miller *et al.* for the cumulative reaction probability, which employs the flux operator, was revealed. Also, making use of the trace form for the cumulative reaction probability, $N(E) = \text{Tr}(\mathbf{S}_{rp}(E)\mathbf{S}_{rp}^\dagger(E))$, we obtained two direct expressions for $N(E)$ in terms of the time-correlation functions. One of them is based on the correlation of the full and product-projected wavepackets, and the other involves the

reactant/product wavepacket correlation functions. The wavepackets are incoming/outgoing in the translational coordinate and form a complete set in an arbitrary basis in the internal coordinates.

One of the new formulations, involving the reactant/product correlation functions, can be readily used with the initial-value semiclassical propagators. The combination of this formulation and the HK propagator for the collinear hydrogen exchange reaction, which has been the traditional testing ground for semiclassical methods, gave the first semi-quantitative semiclassical results for $N(E)$ for this benchmark system. Until now, semiclassical calculation of $N(E)$ has been reported in one dimension only.³⁸

We believe that the general strategy presented here, of reformulating the reactive scattering problem in terms of wavepacket time correlation functions, combined with approximate propagation methods, may make it possible in the future to calculate reaction probabilities and reaction rates for a multitude of chemically important systems.

Appendix A: semiclassical propagator of Herman and Kluk

The propagator, suggested by Herman and Kluk (HK), is the initial value representation propagator with the same semiclassical limit (*i.e.* the stationary phase approximation for $\hbar \rightarrow 0$) as the Schrödinger equation. It is based on the expansion of a wavefunction in terms of Gaussians of a fixed width, whose centers move classically and whose phases are defined by the corresponding classical actions. The propagator converges uniformly,³⁹ it is unitary in the stationary phase approximation, and it is time reversible.⁴⁰

The HK propagator in N dimensions, generalized to include the width parameters as a matrix, is

$$K_{sc}(\mathbf{x}', t; \mathbf{x}, 0) = \frac{1}{(2\pi)^N} \iint d\mathbf{p}_0 d\mathbf{q}_0 R_{pqt} e^{iS_{qpt}} \times g_\gamma(\mathbf{q}_t, \mathbf{p}_t, \mathbf{x}') g_\gamma^*(\mathbf{q}_0, \mathbf{p}_0, \mathbf{x}) \quad (\text{A1})$$

The function

$$g_\gamma(\mathbf{q}_t, \mathbf{p}_t, \mathbf{x}) = \left(\frac{\det(\mathbf{\Gamma})}{\pi^N} \right)^{1/4} \times \exp \left(-\frac{1}{2} (\mathbf{x} - \mathbf{q}_t) \mathbf{\Gamma} (\mathbf{x} - \mathbf{q}_t) + i \mathbf{p}_t \cdot (\mathbf{x} - \mathbf{q}_t) \right) \quad (\text{A2})$$

is a complex Gaussian with the diagonal width matrix $\mathbf{\Gamma} = \{\gamma_{ij}\}$. All γ_i are real and positive. Vectors $\mathbf{q}_0 = (q_0^1, \dots, q_0^N)$ and $\mathbf{p}_0 = (p_0^1, \dots, p_0^N)$ are initial conditions of a classical trajectory at time zero. Vectors $\mathbf{q}_t = (q_t^1, \dots, q_t^N)$ and $\mathbf{p}_t = (p_t^1, \dots, p_t^N)$ are its coordinates and momenta at time t . The classical action is

$$S_{pqt} = \int_0^t [\mathbf{p}_{t'} \cdot \dot{\mathbf{q}}_{t'} - H(\mathbf{p}_{t'}, \mathbf{q}_{t'}, t')] dt' \quad (\text{A3})$$

The prefactor carrying a trajectory stability information is

$$R_{pqt} = \sqrt{\det(\mathbf{B})} \quad (\text{A4})$$

with the matrix elements $\mathbf{B} = \{b_{ij}\}$ being

$$b_{ij} = \frac{1}{2} \left(\sqrt{\frac{\gamma_i}{\gamma_j}} \frac{\partial p_i^1}{\partial p_0^j} + \sqrt{\frac{\gamma_j}{\gamma_i}} \frac{\partial q_j^1}{\partial q_0^i} - i \sqrt{\gamma_i \gamma_j} \frac{\partial q_j^1}{\partial p_0^i} + \frac{i}{\sqrt{\gamma_i \gamma_j}} \frac{\partial p_i^1}{\partial p_0^j} \right) \quad (\text{A5})$$

Eqn. (A5) contains the square root of a complex function: the sign has to be chosen such that R_{pqt} is a continuous function of time.³⁸ The integration goes over all initial values ($\mathbf{q}_0, \mathbf{p}_0$). In theory, the propagator does not depend on the parameters $\{\gamma_{ij}\}$. The choice of γ_i being equal to the width of a wave-

packet to be propagated gives the minimal phase space volume.

The general form for the semiclassical time correlation function of the two states Φ_A and Φ_B is

$$C_{AB}(t) = \iint dx dx' \Phi_B^*(x', 0) K^{sc}(x', t; x, 0) \Phi_A(x, 0)$$

Substituting in the HK expression for the propagator leads to the equation

$$C_{AB}(t) = \iint \frac{dq_0 dp_0}{(2\pi)^N} R_{pqt} e^{iS_{pqt}} \times \int \Phi_B^*(x', 0) g_\gamma(q_t, p_t, x') dx' \times \int g_\gamma^*(q_0, p_0, x) \Phi_A(x, 0) dx \quad (A6)$$

If both wavefunctions, Φ_A and Φ_B , are Gaussians of width $\{\gamma_1, \dots, \gamma_N\}$, i.e.

$$\Phi_{A(B)}(x) = \left(\frac{\det(\Gamma)}{\pi^N} \right)^{1/4} \exp \left(-\frac{1}{2} (x - q_{A(B)}) \times \Gamma (x - q_{A(B)} + ip_{A(B)} \cdot (x - q_{A(B)})) \right) \quad (A7)$$

then the integrals over x and x' are analytical and the correlation function is

$$C_{AB}(t) = \iint \frac{dq_0 dp_0}{(2\pi)^N} \exp \left(-\frac{1}{4} (q_t - q_B) \times \Gamma (q_t - q_B) - \frac{1}{4} (p_t - p_B) \Gamma^{-1} (p_t - p_B) - \frac{i}{2} (q_t - q_B) \cdot (p_t + p_B) + \frac{i}{2} (q_0 - q_A) \times (p_0 + p_A) + iS_{pqt} - \frac{1}{4} (q_0 - q_A) \Gamma (q_0 - q_A) - \frac{1}{4} (p_0 - p_A) \times \Gamma^{-1} (p_0 - p_A) \right) R_{pqt} \quad (A8)$$

Appendix B: projection operator approach to the cumulative reaction probability

In this section, starting from the standard definition of the S -matrix given by eqn. (8), we derive a formula for the cumulative reaction probability, $N(E)$, in terms of projection operators. The formula is a simple variant of the trace expression (5), and we will show the equivalence explicitly. We will begin with a number of preliminary relationships.

The occupation of the product region is often characterized by the Heaviside function $h(s)$ defined in eqn. (27). Its commutator with the full Hamiltonian H defines the symmetrized flux operator

$$\bar{F} = \frac{1}{2} (F + F^\dagger) = \frac{1}{2} \left(\delta(s) \frac{p}{m} + \frac{p}{m} \delta(s) \right) = i[H, h(s)] \quad (B1)$$

The operator \hat{P}^+ of eqn. (26), projecting onto the states that form products in the infinite future, is also defined in terms of $h(s)$ as

$$\hat{P}^+ = \sum_\beta \int_0^\infty dE |\psi_{\beta,E}^- \rangle \langle \psi_{\beta,E}^-| = \lim_{t \rightarrow \infty} e^{iHt} h(s) e^{-iHt}$$

There is another projection operator:

$$\hat{P}^- = \hat{P}^{+*} = \sum_\beta \int_0^\infty dE |\psi_{\beta,E}^+ \rangle \langle \psi_{\beta,E}^+| = \lim_{t \rightarrow -\infty} e^{iHt} h(s) e^{-iHt} \quad (B2)$$

which projects onto products in the infinite past.[¶] Its action on the incoming wavepacket is trivial, $\hat{P}^- |\Phi_\alpha^+ \rangle = 0$.

Using eqns. (13) and (B1), and definitions (26) and (B2) we can establish the relation between the projection and the flux operators:

$$(2\pi)^2 \delta(E - H) \bar{F} \delta(E - H) = \int_{-\infty}^\infty dt e^{iHt} i[H, h(s)] e^{-iHt} \int_{-\infty}^\infty dt^- e^{-i(H-E)t^-} = \int_{-\infty}^\infty dt \frac{d}{dt} \{ e^{iHt} h(s) e^{-iHt} \} \int_{-\infty}^\infty dt^- e^{-i(H-E)t^-} = \left(\lim_{t \rightarrow \infty} e^{iHt} h(s) e^{-iHt} - \lim_{t \rightarrow -\infty} e^{iHt} h(s) e^{-iHt} \right) \times 2\pi \delta(E - H) = 2\pi (\hat{P}^+ - \hat{P}^-) \delta(E - H) \quad (B3)$$

In the intermediate steps of the derivation we made the substitution $t^- = \tau - t$. Eqn. (B3) gives

$$(\hat{P}^+ - \hat{P}^-) \delta(E - H) = 2\pi \delta(E - H) \bar{F} \delta(E - H) \quad (B4)$$

providing a relationship between the projection and the flux operators that will be used below. Using the definition of P^+ in terms of energy eigenfunctions, eqn. (22), we may develop an energy-domain version of eqn. (B4):

$$\sum_\beta \int_0^\infty dE' (|\psi_{\beta,E'}^- \rangle \langle \psi_{\beta,E'}^-| - |\psi_{\beta,E'}^+ \rangle \langle \psi_{\beta,E'}^+|) \delta(E - H) = \sum_\beta (|\psi_{\beta,E}^- \rangle \langle \psi_{\beta,E}^-| - |\psi_{\beta,E}^+ \rangle \langle \psi_{\beta,E}^+|) = \delta(E - H) \sum_\beta \int_0^\infty \int_0^\infty dE' dE'' \times (|\psi_{\beta,E'}^- \rangle \langle \psi_{\beta,E''}^-| - |\psi_{\beta,E'}^+ \rangle \langle \psi_{\beta,E''}^+|) \delta(E - H)$$

Thus, the flux operator can be represented as

$$\bar{F} = \frac{1}{2\pi} \sum_\beta \int_0^\infty \int_0^\infty dE' dE'' \times (|\psi_{\beta,E'}^- \rangle \langle \psi_{\beta,E''}^-| - |\psi_{\beta,E'}^+ \rangle \langle \psi_{\beta,E''}^+|) \quad (B5)$$

In other words, we have the spectral representation of the flux operator

$$\bar{F} = \lambda |f\rangle \langle f| - \lambda |f^*\rangle \langle f^*|$$

which has two nonzero eigenvalues λ and $-\lambda$:

$$\bar{F} |f\rangle = \lambda |f\rangle, \quad \bar{F} |f^*\rangle = -\lambda |f^*\rangle, \quad \lambda = (2\pi)^{-1}$$

For internal label $\beta = [0 \dots N]$ the first flux eigenvector is expressed as

$$|f\rangle = \left(\int_0^\infty dE' |\psi_{0,E'}^- \rangle, \dots, \int_0^\infty dE' |\psi_{N,E'}^- \rangle \right)$$

and the second eigenvector is its complex conjugate. This form of \bar{F} is reminiscent of the representation of the flux operator in a finite basis set.^{41,42} However, now we can see that

[¶] Note, that energy eigenfunctions $|\psi_{\beta,E}^+ \rangle$ are orthogonal to $|\psi_{\alpha,E}^+ \rangle$, since $\langle \phi_\beta^* | \phi_\alpha^+ \rangle = 0$ for wavepackets with arbitrary energy expansion coefficients.

the spectral representation of \bar{F} is independent of the specific choice of the characteristic function $\chi(s)$ in eqn. (B1), as long as \bar{F} is defined as the commutator $\bar{F} = i[H, \chi(s)]$, and the function $\chi(s)$ has the same asymptotic behavior as the Heaviside function $h(s)$

$$\lim_{s \rightarrow \infty} \chi(s) = 1, \quad \lim_{s \rightarrow -\infty} \chi(s) = 0$$

We are now ready for the actual derivation. We begin by noting that the cumulative reaction probability can be expressed as a trace of the reactive S -matrix, denoted S_{rp} ,

$$N(E) = \text{Tr}\{S_{rp}(E)^\dagger S_{rp}(E)\} \quad (\text{B6})$$

Using the definition of the S -matrix elements (8) together with eqn. (22) and permutating under the trace, we get

$$\begin{aligned} N(E) &= \text{Tr} \left(\int \int dE' dE'' S^\dagger(E) \delta(E - E') S(E') \delta(E' - E'') \right) \\ &= \text{Tr} \left(\int dE'' \langle \psi_{\alpha, E}^+ | \hat{P}^+ | \psi_{\alpha, E''}^+ \rangle \right) \\ &= \text{Tr} \left((\hat{P}^+ - \hat{P}^-) \int \int dE'' dE' | \psi_{\alpha, E''}^+ \rangle \delta(E - E') \langle \psi_{\alpha, E'}^+ | \right) \\ &= \text{Tr} \left((\hat{P}^+ - \hat{P}^-) \delta(E - H) \int \int dE'' dE' | \psi_{\alpha, E''}^+ \rangle \langle \psi_{\alpha, E'}^+ | \right) \end{aligned} \quad (\text{B7})$$

The operator P^- was introduced, since $P^- |\psi^+\rangle = 0$. Now, adding eqn. (B7) to its complex conjugate ($\hat{P}^+ - \hat{P}^- = -(\hat{P}^+ - \hat{P}^-)^*$), and using eqn. (B5), we obtain our final formula

$$N(E) = \pi \text{Tr}((\hat{P}^+ - \hat{P}^-) \delta(E - H) \bar{F}) \quad (\text{B8})$$

Eqn. (B8) is an alternative trace expression for $N(E)$. Using eqn. (B4) in eqn. (B8), we immediately recover the expression of Miller *et al.*¹

$$N(E) = 2\pi^2 \text{Tr}(\delta(E - H) \bar{F} \delta(E - H) \bar{F}) \quad (\text{B9})$$

Using the properties $\hat{P}^{+*} = \hat{P}^-$, $\bar{F} = (F + F^\dagger)/2 = -\bar{F}^*$ and permutation under the trace, the Boltzmann average of eqn. (B8) gives

$$\begin{aligned} k(T)Q(T) &= \pi \text{Tr} \left(\int dE (\hat{P}^+ - \hat{P}^-) \delta(E - H) \hat{F} e^{-E/kT} \right) \\ &= 2\pi \mathcal{R} \{ \text{Tr}(\hat{P}^+ F e^{-H/kT}) \} \end{aligned} \quad (\text{B10})$$

which is another well-known expression for the reaction rate.¹ Note that we did not try to evaluate the trace in a complete

set of states, but introduced the trace in the beginning. Thus, the present derivation is valid in the presence of bound states.

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